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**Thermoplastic Polyester Composition and Film**

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**(54) [Title of the Invention]**

**Thermoplastic Polyester Composition and Film**

**(57) [Summary]**

**[Constitution]** A thermoplastic polyester composition and film, characterized by containing aluminum oxide particles that have a  $\theta$ -type crystal structure, and a thermoplastic polyester in which an aromatic dicarboxylic acid is used as a principal acid component, and an aliphatic glycol is used as a principal glycol component.

**[Effect]** Films, fibers, and other molded articles obtained from the thermoplastic polyester composition of the present invention have high shear strength; exhibit exceptional durability in these applications; are highly abrasion resistant, particularly in the calendering step when magnetic tape is manufactured; and are preferably used as a support for magnetic tape.

## **[Claims]**

**[Claim 1]** A thermoplastic polyester composition and film, characterized by containing aluminum oxide particles that have a  $\theta$ -type crystal structure, and a thermoplastic polyester in which an aromatic dicarboxylic acid is used as a principal acid component, and an aliphatic glycol is used as a principal glycol component.

**[Claim 2]** A film comprising the thermoplastic polyester composition of Claim 1.

## **[Detailed Description of the Invention]**

### **[0001]**

**[Field of Industrial Utilization]** The present invention relates to a thermoplastic polyester composition and a film. In further detail, the present invention relates to a thermoplastic polyester composition that contains aluminum oxide having a specific crystal structure, and that affords exceptional calenderability when magnetic tapes are manufactured from films made therefrom.

### **[0002]**

**[Prior Art]** Thermoplastic polyesters such as polyethylene terephthalate generally have exceptional dynamic characteristics, and are extensively used in films, fibers, and other molded articles. Inert particles are normally admixed with these polyesters, and irregularities are imparted to the surfaces of such molded articles in order to provide slidability thereto. Although various types of inert particles exist, problems are generally encountered with their use owing to a lack of affinity with the polyester, and diminished abrasion-resistance.

**[0003]** Surface treatments have been investigated in the past in order to resolve such problems, such as those proposed in Japanese Laid-Open Patent Applications (Kokai) 63-221158 and 63-280763 (modification of colloidal silica particle surfaces with glycol groups); 63-312345 (modification of colloidal silica particle surfaces with coupling agents); and 62-235353 (surface treatment of calcium carbonate particles using phosphorus compounds).

**[0004]** However, particle shedding persists with magnetic tape or other applications involving repeated abrasion, despite such well-known methods having been performed. Accordingly, recent proposals have focused on the use of unique particles, such as aluminum oxide particles, which have had a significant effect on abrasion-resistance, as has been proposed in Japanese

Laid-Open Patent Applications (Kokai) 2-129230 (delta-type aluminum oxide particles), 2-38444 (aluminum oxide particles), and the like.

[0005] However, the findings proposed in this literature have remained inadequate as regards inhibiting abrasion of the film surface that occurs, for example, due to friction between the calender rolls and the film when a calendering step is employed in the manufacture of magnetic tape in which a polyester film is used as a support.

[0006] When blank tapes are dubbed, tapes are rewound in a videotape deck, or other similar activities are performed with magnetic tape, the travelling surface of the tape normally remains in contact with a guide pin as it passes at high speed. During such action, the travelling surface of the tape will be abraded as a result of very fine irregularities in the surface of the guide pin, if its surface has not been machined to a smooth finish, and a fine whitish powder will be produced as a result. This powder will adhere to the magnetic layer side of the tape when it is rewound, creating undesirable results during recording or playback, such as image dropout. However, image dropout lasts for only a very short amount of time, and is not a contributing factor towards long-duration image dropout, which is a serious drawback to practical application.

[0007] On the other hand, when magnetic tape is manufactured, an uncured magnetic layer is applied to a polyester film support, and calendering is performed to smoothen the surface. The travelling surface of the tape is abraded due to the friction encountered when the tape passes between the calender rolls during such a procedure. The abraded material adheres to the magnetic layer, and causes problems such as long-duration image dropout, which is a serious drawback in terms of practical application. The state of abrasion during the calendering step may be examined by means of passing a single film between the calender rolls, and then observing the state in which the abraded material has adhered to the rolls.

[0008] The prior art proposed in the aforementioned specifications has been effective in limiting the generation of the very fine powder; however, and as has been described in the foregoing, the prior art has been ineffective in inhibiting film abrasion that occurs in the calendering step when magnetic tape is manufactured, and in resolving long-duration image dropout, which is a serious drawback in terms of practical application.

[0009]

**[Problems to Be Solved by the Invention]** It is an object of the present invention to provide a thermoplastic polyester film that does not suffer from abrasion in the calendering step when

magnetic tape is manufactured, as has been described in the foregoing, and that makes it possible to manufacture exceptionally calender-resistant magnetic tape devoid of image dropout, which is a major drawback in terms of practical application and which is caused when abraded material adheres to the tape.

[0010]

**[Means Used to Solve the Above-Mentioned Problems]** The aforesaid object of the present invention may be achieved by means of a thermoplastic polyester composition and film characterized in containing aluminum oxide particles that have a  $\theta$ -type crystal structure, and a thermoplastic polyester in which an aromatic dicarboxylic acid is used as a principal acid component, and an aliphatic glycol is used as a principal glycol component.

[0011] A variety of methods are known for synthesizing the  $\theta$ -type aluminum oxide particles of the present invention; e.g., sintering carbonates that have been neutralized with alum, sintering hydroxides obtained by means of spark discharging metallic aluminum under water, or sintering hydroxides formed as a result of the hydrolysis of aluminum alkoxides.

[0012] The crystal structure of the  $\theta$ -type aluminum oxide obtained by means of the aforementioned methods may be identified with the help of X-ray diffraction analysis.

[0013] The primary particle diameter, as expressed in terms of specific surface area, is preferably  $10 \text{ m}^2/\text{g}$  or larger, and more preferably  $50 \text{ m}^2/\text{g}$  or larger.  $600 \text{ m}^2/\text{g}$  is even more preferable, while  $50$  to  $200 \text{ m}^2/\text{g}$  is especially preferable.

[0014] However, particles of such fineness have a marked tendency to aggregate, and normally form secondary particles by means of aggregating in slurries or polymers. Bulky particles may form, depending on the extent to which aggregation proceeds, and these regions will be shed due to abrasion encountered when films or fibers made with such materials are in motion.

[0015] An example of a method for obtaining the composition of the present invention involves the use of a slurry that has been produced by means of subjecting  $\theta$ -type aluminum oxide particles to a wet dispersion process in the presence of a solvent. This slurry is added to a polyester polymerization reaction or the like, and the reaction is completed.

[0016] Although the particles will aggregate and form secondary particles in the slurry that has been obtained by means of the wet dispersion process, the secondary particle diameter will be extremely small, no bulky aggregates will form, and a uniformly dispersed state will result. The

term "secondary particle diameter" herein refers to the mean size corresponding to the circles observed on 1,000 particles using a transmission electron microscope.

[0017] The viscosity will increase when the wet dispersion process is performed in the presence of a solvent, and therefore the concentration of aluminum oxide particles is preferably 1 to 50 wt%, and more preferably 3 to 30 wt%.

[0018] There are no particular limitations as to the solvent used therein, but a glycol component such as used as a principal raw material or copolymerizing component of the polyester is preferred, taking into account that this solvent is to be added subsequently to the polyester. Specific examples include ethylene glycol, tetramethylene glycol, hexamethylene glycol, diethylene glycol, propylene glycol, butane diol, neopentyl glycol, polyoxyalkylene glycol, *p*-xylylene glycol, 1,4-cyclohexanedimethanol, and 5-sodium sulforesorcin. Examples of the dispersion process to be performed herein include ordinary stirring, ultrasonic treatment, and dispersion with a medium, among which the latter (e.g., a sand grinder) is preferred.

[0019] Performing the wet dispersion process on the  $\theta$ -type aluminum oxide particles in the presence of a solvent will dramatically improve dispersibility, and the secondary particle diameter may be suitably selected according to the intended use of molded articles formed from the thermoplastic polyester composition. Too large a diameter will result in the formation of bulky protrusions in the molded article when the composition is used in films or fibers; therefore, the diameter is preferably 5.0  $\mu\text{m}$  or less, more preferably 3.0  $\mu\text{m}$  or less, and even more preferably 0.01  $\mu\text{m}$  or less. A diameter of 0.01 to 1  $\mu\text{m}$  is especially preferred.

[0020] The amount of particles to be added should be determined based on the same reasoning. In other words, too great an amount of aluminum oxide particles will result in the formation of bulky protrusions in the molded article when the composition is used in films or fibers; therefore, the total amount per 100 weight parts of thermoplastic polyester is preferably 0.01 to 30 weight parts, and more preferably 0.05 to 20 weight parts. An amount of 0.05 to 10 weight parts is especially preferred.

[0021] Specific examples of the aromatic dicarboxylic acid of the present invention include terephthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, and 5-sodiumsulfoisophthalic acid. Specific examples of the aliphatic glycol of the present invention include ethylene glycol, diethylene glycol, propylene glycol, butane diol, tetramethylene glycol, hexamethylene glycol, neopentyl glycol, and polyoxyalkylene glycol.

[0022] Specific examples of the thermoplastic polyester that comprises such aromatic dicarboxylic acids and aliphatic glycols include polyethylene terephthalate, polybutylene terephthalate, and polyethylene-2,6-naphthalate. The polyester may be a homopolyester or, if present in small amounts, a copolyester containing a copolymerizing component. Examples of such copolymerizing components include adipic acid, sebacic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, 5-sodiumsulfoisophthalic acid, and other dicarboxylic acid components; trimellitic acid, pyromellitic acid, and other polycarboxylic acid components; and tetramethylene glycol, hexamethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, polyoxyalkylene glycol, *p*-xylylene glycol, 1,4-cyclohexanedimethanol, 5-sodium sulforesorcin, and other diol components.

[0023] The degree of polymerization of such thermoplastic polyesters is preferably 0.30 or higher in terms of the limiting viscosity  $[\eta]$  measured once the polyester has been dissolved in *o*-chlorophenol. It is moreover preferable for the carboxyl terminal group content of the thermoplastic polyester to be 20 eq/t to 100 eq/t.

[0024] Additives such as antioxidants and well-known particles used to improve take-up and running characteristics during machining or film manufacture may be added, provided that the effect of the present invention will not be adversely affected. Examples include calcium carbonate; kaolin; talc; magnesium carbonate; barium carbonate; calcium carbonate [sic]; barium sulfate; lithium phosphate; calcium phosphate; magnesium phosphate; silicon oxide; titanium oxide; lithium fluoride; calcium succinate; one or more metal compounds selected from among terephthalates or other compounds of calcium, barium, zinc, manganese, or the like; and particulate phenols and ureas, as well as particulate crosslinked polymers obtained from homopolymers, copolymers, or other compounds of vinyl monomers such as divinyl benzene, styrene, acrylic acid, methacrylic acid, or alkyl esters thereof.

[0025] The slurry produced by means of subjecting  $\theta$ -type aluminum oxide particles to a wet dispersion process in the presence of a solvent should be added to the polymerization reaction system of the thermoplastic polyester at any time before the polymerization reaction is complete, but is preferably added from before transesterification and until depressurization of the polycondensation reaction has begun.

[0026] Films that are in accordance with the object of the present patent application may be fabricated from the resulting thermoplastic composition by means of any known method. In such

instances, it is possible for all of the film layers to comprise the composition of the invention according to the present application, as well as for the film to be a composite of two or more layers, in which at least one surface comprises the composition of the invention according to the present application.

**[0027]**

**[Working Examples]** The present invention shall be described in detail below with reference to working and comparative examples.

**[0028]** (1) Evaluation of specific surface area of aluminum oxide particles

The measurements (in  $\text{m}^2/\text{g}$ ) were performed according to a common BET method.

**[0029]** (2) Evaluation of secondary particle diameter of aluminum oxide particles

Aluminum oxide particles were compounded in a polyester, and the resulting compound was cut into ultra-thin (thickness:  $0.2\ \mu\text{m}$ ) pieces. The pieces were then observed under a transmission electron microscope, and the secondary particle diameter was evaluated based on the mean diameter of the surface area ( $\mu\text{m}$ ) covered by 1,000 aggregated secondary particles.

**[0030]** (3) Evaluation of abrasion-resistance

Biaxially oriented films were fabricated from the resulting polyester compositions according to the method described in the working examples, and slit into narrow-width tapes. A roll of this tape was brought into frictive contact with a guide roll (made from SUS-304 stainless steel) under constant tension, at high speed, and for an extended period of time. The abrasion-resistance was ranked as described hereunder according to the quantity of white powder that had amassed on the surface of the guide roll. A rank of "1" was regarded as being satisfactory.

- 1: No white powder present
- 2: Some white powder present
- 3: Appreciable amount of white powder present

**[0031]** (4) Evaluation of surface irregularities

The resulting polyester compositions were biaxially stretched into films using a common method. The centerline-average roughness (Ra) of these films was measured according to JIS B-0601 using a Surfcom surface roughness measuring device, under the following conditions: probe diameter:  $2\ \mu\text{m}$ ; load: 70 mg; standard measuring length: 0.25 mm; cut-off: 0.08 mm.



**[0032] (5) Evaluation of calenderability**

The obtained film was cut into 300 mm-wide strips and calendered at a temperature of 70°C and a linear pressure of 200 kg/cm, using a miniature test calendering apparatus (comprising a five-level system with steam rolls and nylon rolls, with the nylon rolls being in contact with the base film surface). The aforementioned process lasted a total of 5,000 m of film, after which any white powder that had formed during the process and had adhered to the nylon rolls was removed with adhesive tape. The quantity of white powder formations having a size of 10  $\mu\text{m}$  or larger was observed under a microscope, and ranked as described hereunder. A ranking of "1" or "2" was regarded as being satisfactory.

- 1: 0 to 15 white powder formations per square meter
- 2: 16 to 30 white powder formations per square meter
- 3: 31 or more white powder formations per square meter

**[0033] Working Example 1**

10 weight parts of  $\theta$ -type aluminum oxide particles having a specific surface area of 146  $\text{m}^2/\text{g}$  (according to BET) and 90 weight parts of ethylene glycol were mixed and dispersed using a sand grinder, resulting in 100 weight parts of a  $\theta$ -type aluminum oxide particle/ethylene glycol slurry (A).

**[0034]** Meanwhile, 0.05 weight parts of magnesium acetate was added as a catalyst to 100 weight parts of dimethyl terephthalate and 64 weight parts of ethylene terephthalate, and transesterification was performed. The resulting reaction product was admixed with 2.5 weight parts of an already prepared slurry (A), 0.03 weight parts of antimony oxide as a catalyst, and 0.03 weight parts of trimethyl phosphate as a heat-resistance stabilizer. A polycondensation reaction was performed, resulting in a polyethylene terephthalate composition with a limiting viscosity of 0.619. The composition had a secondary particle diameter of 0.22  $\mu\text{m}$ , as determined using a transmission electron microscope.

**[0035]** The polyethylene terephthalate composition was melt-extruded at 290°C, and subsequently stretched 300% in both the longitudinal and transverse directions at 90°C. A heat treatment was then performed for 15 sec at 220°C, resulting in a 15- $\mu\text{m}$ -thick biaxially stretched polyethylene terephthalate film.

[0036] On evaluation, the film was shown to have an Ra of 0.011  $\mu\text{m}$ , an abrasion-resistance ranking of 2, and a calenderability ranking of 1, which was a highly satisfactory assessment overall.

**[0037] Working Example 2**

10 weight parts of calcite-type calcium carbonate particles having an average particle diameter of 0.63  $\mu\text{m}$ , and 90 weight parts of ethylene glycol were mixed and dispersed using a sand grinder. The resulting mixture was filtered with a filter that had an absolute filtration accuracy of 5  $\mu\text{m}$ , resulting in 100 weight parts of a calcite-type calcium carbonate particle/ethylene glycol slurry (B).

[0038] A biaxially stretched film was obtained in the same manner as described in Working Example 1, with the exception that the BET specific surface area of the  $\theta$ -type aluminum oxide particles was changed from 146  $\text{m}^2/\text{g}$  to 85  $\text{m}^2/\text{g}$ , and that two weight parts of slurry (B), which had been obtained as described in the foregoing, was added simultaneously with the  $\theta$ -type aluminum oxide particle/ethylene glycol slurry.

[0039] On evaluation, the film was shown to have an Ra of 0.017  $\mu\text{m}$ , an abrasion-resistance ranking of 2, and a calenderability ranking of 2, which was a satisfactory assessment overall.

**[0040] Working Example 3**

Polyethylene terephthalate with a limiting viscosity of 0.622 and containing no particles was coextruded with the polymer as described in Working Example 1, with the polymer of Working Example 1 being laminated to a thickness of 1  $\mu\text{m}$  on both sides of the particle-free polyethylene terephthalate, and resulting in a 14  $\mu\text{m}$ -thick biaxially oriented laminated film.

[0041] On evaluation, the film was shown to have an Ra of 0.010  $\mu\text{m}$ , an abrasion-resistance ranking of 2, and a calenderability ranking of 1, which was a highly satisfactory assessment overall.

**[0042] Working Example 4**

A 14  $\mu\text{m}$ -thick film was obtained in the identical manner as described in Working Example 3, with the exception that the polymer of Working Example 2 was used instead of the polymer of Working Example 1, and laminated on both sides of the particle-free polyethylene terephthalate.

[0043] On evaluation, the film was shown to have an abrasion-resistance ranking of 2, and a calenderability ranking of 2, which was a satisfactory assessment overall.

**[0044] Working Example 5**

A slurry comprising 10 weight parts of spherical organic particles having an average particle diameter of 0.45  $\mu\text{m}$  (divinyl benzene/vinyl benzene (80/20) copolymer) and 90 weight parts of water was melt-kneaded with polyethylene terephthalate using a vented twin-screw kneader, resulting in a polyethylene terephthalate composition in which the final content of the aforementioned spherical organic particles was 1 wt%.

[0045] Next, 20 weight parts of the aforementioned polyethylene terephthalate composition that contained 1 wt% organic particles were melt-kneaded with 80 weight parts of a polyethylene terephthalate composition that had been obtained in a manner identical to that as described in Working Example 1, with the exception that the BET specific surface area of the  $\theta$ -type aluminum oxide particles was changed from 146  $\text{m}^2/\text{g}$  to 85  $\text{m}^2/\text{g}$ . The resulting molten mixture was then formed into a 14  $\mu\text{m}$ -thick biaxially stretched laminated film in a manner identical to that as described in Working Example 1.

[0046] On evaluation, the film was shown to have an Ra of 0.019  $\mu\text{m}$ , an abrasion-resistance ranking of 2, and a calenderability ranking of 1, which was a highly satisfactory assessment overall.

**[0047] Working Example 6**

A 14  $\mu\text{m}$ -thick film was obtained in the identical manner as described in Working Example 3, with the exception that the molten mixture of Working Example 4 that contained two polyethylene terephthalate compositions was used instead of the polymer of Working Example 1, and laminated on both sides of the polyethylene terephthalate that contained no particles.

[0048] On evaluation, the film was shown to have an Ra of 0.018  $\mu\text{m}$ , an abrasion-resistance ranking of 2, and a calenderability ranking of 1, which was a highly satisfactory assessment overall.

**[0049] Comparative Example 1**

10 weight parts of  $\delta$ -type aluminum oxide particles having a BET specific surface area of 108  $\text{m}^2/\text{g}$ , and 90 weight parts of ethylene glycol were mixed and then dispersed using a sand grinder, resulting in 100 weight parts of a  $\delta$ -type aluminum oxide particle/ethylene glycol slurry (C).

[0050] Meanwhile, 0.05 weight parts of magnesium acetate was added as a catalyst to 100 weight parts of dimethyl terephthalate and 64 weight parts of ethylene glycol, and transesterification was performed. The resulting reaction product was admixed with 5 weight parts of an already prepared slurry (C), 0.03 weight parts of antimony oxide as a catalyst, and 0.03 weight parts of trimethyl phosphate as a heat-resistance stabilizer. A polycondensation reaction was performed, resulting in a polyethylene terephthalate composition with a limiting viscosity of 0.619. The secondary particle diameter was 0.18  $\mu\text{m}$ , as determined using a transmission electron microscope. The polyethylene terephthalate composition was melt-extruded at 290°C, and subsequently stretched 300% in both the longitudinal and transverse directions at 90°C. A heat treatment was then performed for 15 sec at 220°C, resulting in a 15- $\mu\text{m}$ -thick biaxially stretched polyethylene terephthalate film.

[0051] On evaluation, the film was shown to have an Ra of 0.011  $\mu\text{m}$ , an abrasion-resistance ranking of 2, and a calenderability ranking of 3, which was an unsatisfactory assessment overall.

#### [0052] Comparative Example 2

A biaxially stretched film was obtained in the same manner as described in Comparative Example 1, with the exception that  $\gamma$ -type aluminum oxide particles having a specific surface area of 138  $\text{m}^2/\text{g}$  were used instead of the  $\delta$ -type aluminum oxide particles. On evaluation, the film was shown to have an abrasion-resistance ranking of 2 and a calenderability ranking of 3, which was an unsatisfactory assessment overall.

#### [0053]

[Effect of the Invention] Molded articles fabricated from films or fibers obtained from the thermoplastic polyester composition of the present invention have a high shear strength; exhibit exceptional durability in these applications; are highly abrasion-resistant, particularly in the calendering step when magnetic tape is manufactured; and may preferably be used as supports for magnetic tape.